

## SUPPLEMENTAL DATA

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# Sequestration and Transformation in Chemically Enhanced Treatment Wetlands: DOC, DBPPs, and Nutrients

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## Kinetic Model Derivation to Model DOC

Mass In = Mass out surface water + change in mass + loss to infiltration

$$C_x Q_x = C_{x+\Delta x} Q_{x+\Delta x} + \frac{\Delta C}{\Delta t} V + \Delta Q \left( \frac{C_x + C_{x+\Delta x}}{2} \right) \quad \text{Eq. S1}$$

Where

C = Concentration, represented for different locations ( $x, x+\Delta x$ ) along the reactor

Q = flow, represented for different locations along the reactor

t = time and

V = volume, equivalent to height ( $h$ ) times width ( $w$ ) times length ( $\Delta x$ ) of reactor

$$C_x Q_x = C_{x+\Delta x} Q_{x+\Delta x} + \frac{\Delta C}{\Delta t} h w \Delta x + \Delta Q \left( \frac{C_x + C_{x+\Delta x}}{2} \right) \quad \text{Eq. S2}$$

Assume  $C_x$  approaches  $C_{x+\Delta x}$  as  $\Delta x$  approaches zero, equation (Eq. S2) becomes

$$C_x Q_x = C_{x+\Delta x} Q_{x+\Delta x} + \frac{\Delta C}{\Delta t} h w \Delta x + C_{x+\Delta x} \Delta Q \quad \text{Eq. S3}$$

And can be rearranged to become

$$C_x Q_x = C_{x+\Delta x} (\Delta Q + Q_{x+\Delta x}) + \frac{\Delta C}{\Delta t} h w \Delta x \quad \text{Eq. S4}$$

From the water balance:

$$\Delta Q + Q_{x+\Delta x} = Q_x \quad \text{Eq. S5}$$

Thus, the mass balance becomes --

$$C_x Q_x = C_{x+\Delta x} Q_x + \frac{\Delta C}{\Delta t} h w \Delta x \quad \text{Eq. S6}$$

$$-(C_{x+\Delta x} - C_x) Q_x = \frac{\Delta C}{\Delta t} h w \Delta x \quad \text{Eq. S7}$$

Reorganizing equation (Eq. S7) yields --

$$-(\Delta C) Q_x = \frac{\Delta C}{\Delta t} h w \Delta x \quad \text{Eq. S8}$$

As  $\Delta C$  approaches  $\partial C$  and  $\Delta t$  approaches  $\partial t$ , the equation becomes --

$$-(\partial C) Q_x = \frac{\partial C}{\partial t} h w \partial x \quad \text{Eq. S9}$$

Changes in C are assumed to follow first order kinetics:

$$\frac{\partial C}{\partial t} = K C \quad \text{Eq. S10}$$

Where K is the rate constant

Inserting the first order into equation (Eq. S10), allows equation (Eq. S9) to become --

$$-(\partial C) Q_x = K C h w \partial x$$

Which can be reorganized to successively become --

$$-\left(\frac{\partial C}{C}\right) Q_x = Khw\partial x \quad \text{Eq. S11}$$

$$Q_x = wh \frac{\partial x}{\partial t} \quad \text{Eq. S12}$$

$$-\left(\frac{\partial C}{C}\right) = K\partial t \quad \text{Eq. S13}$$

Applying integrands to both sides of the equation with the limits of  $C_{pd}$  (concentration at post-dosed inflow locations) at time zero and  $C_o$  (concentration at outflow) at the end of the wetland, the hydraulic retention time (HRT), equation (Eq. S13) becomes --

$$\int_{pd}^{C_o} \left(\frac{\partial C}{C}\right) = \int_0^{HRT} K\partial t \quad \text{Eq. S14}$$

Allows integration of equation (Eq. S14) to become --

$$\ln \frac{C_o}{C_{pd}} = -K(HRT) \quad \text{Eq. S15}$$

Which can be again reorganized to become --

$$C_o = C_{pd} e^{-K(HRT)} \quad \text{(Eq. 1 in the main text)}$$

### Addition of Temperature Relationships

Microbial relationships have been shown to follow a modified Arrhenius relationship (EPA, 1993; Metcalf and Eddy, 1979) regarding a temperature effect such that

$$K_T = K_{20} \theta^{T-20} \quad \text{Eq. S17}$$

With

$K_T$  = rate constant at temperature T in °C

$K_{20}$  = rate constant at temperature 20 °C

$\theta$  = temperature dependency of rate

Integrating that relationship equation (Eq. S17) yields --

$$C_o = C_{pd} e^{-K_{20} \theta^{T-20} (HRT)} \quad \text{(Eq. 2 in the main text)}$$

### Addition of Desorption from Flocculant

Flocculants remove DOC and other WQCC through co-precipitation and removal have shown to be reversible (Chen et al 2014). Thus, the mass of DOC removed can be described by –

$$z_{me} = z_r + z_{ir} \quad \text{Eq. S19}$$

Where

$z_{me}$  = total mass removed during coagulation

$z_r$  = mass removed reversibly

$z_{ir}$  = mass removed irreversibly

If the organic carbon is released after coagulation, then that amount relates to the percentage of the total removed during coagulation that is reversible

$$z_r = \%_{Me} z_{Me} \quad \text{Eq. S20}$$

Where

$\%_{Me}$  = the percent reversible removal specific to the coagulation used

$z_{Me}$  = total mass removed during coagulation

Replacing (Eq. S20) mass terms for concentration gives --

$$C_r = \%_{Me} \Delta C_{Me} \quad \text{Eq. S21}$$

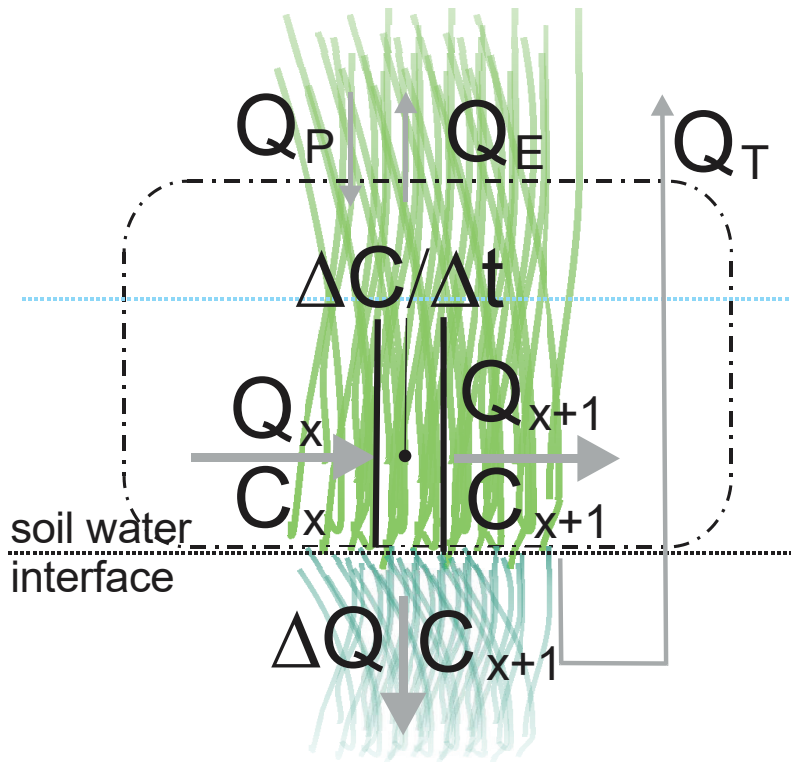
Addition of a temperature dependency term give –

$$C_r = \%_{Me} \Delta C_{Me} \times \theta_{Me}^{T-20} \quad \text{(Eq. 3 in the main text)}$$

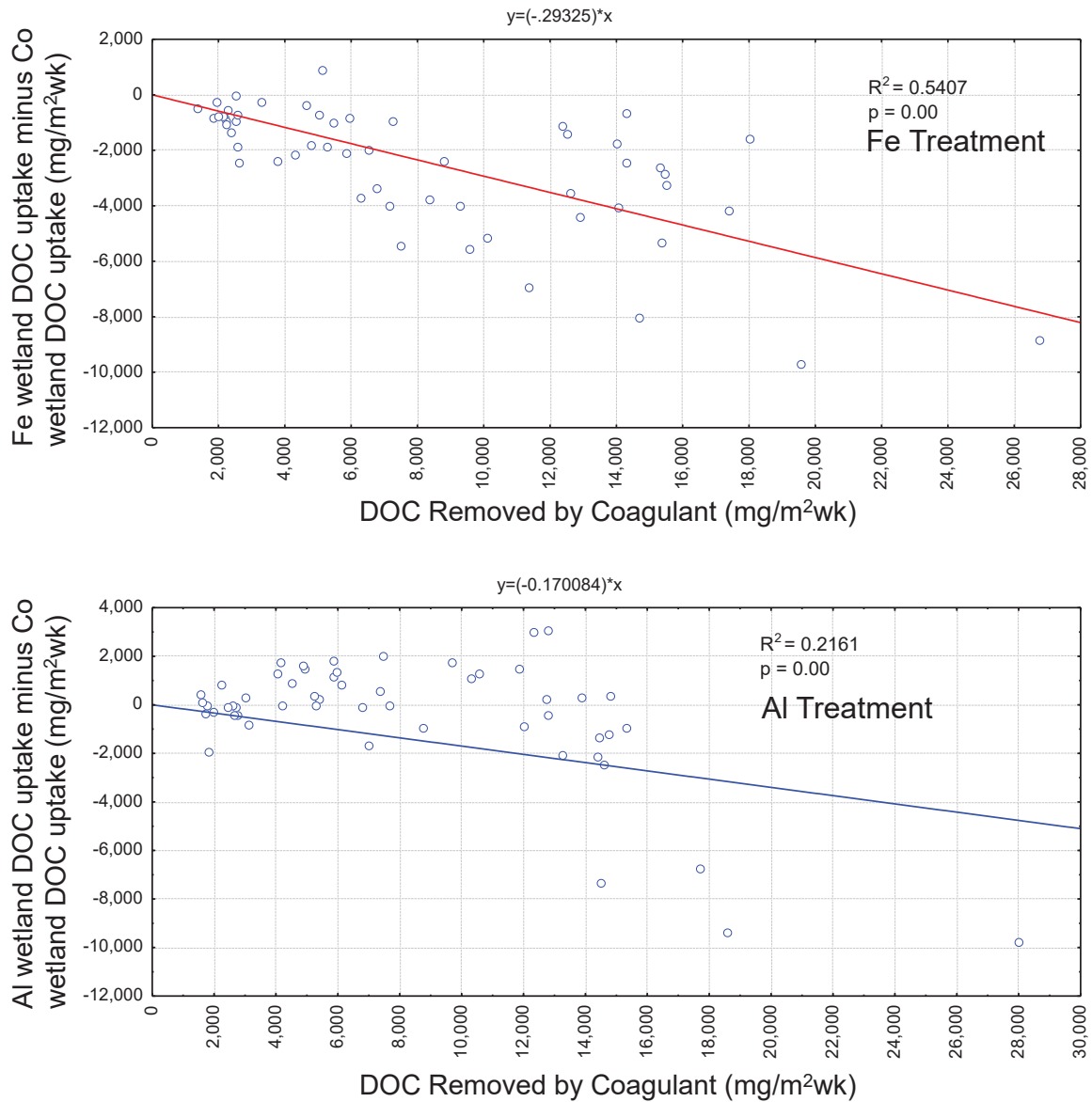
Combining equation (2) for wetland processes and equation (3) for desorption processes, the outflow concentration from the wetlands can be described as --

$$C_o = C_{pd} e^{-K_{20} \theta^{T-20} (HRT)} + \%_{Me} \Delta C_{Me} \times \theta_{Me}^{T-20} \quad \text{(Eq. 4 in the main text)}$$

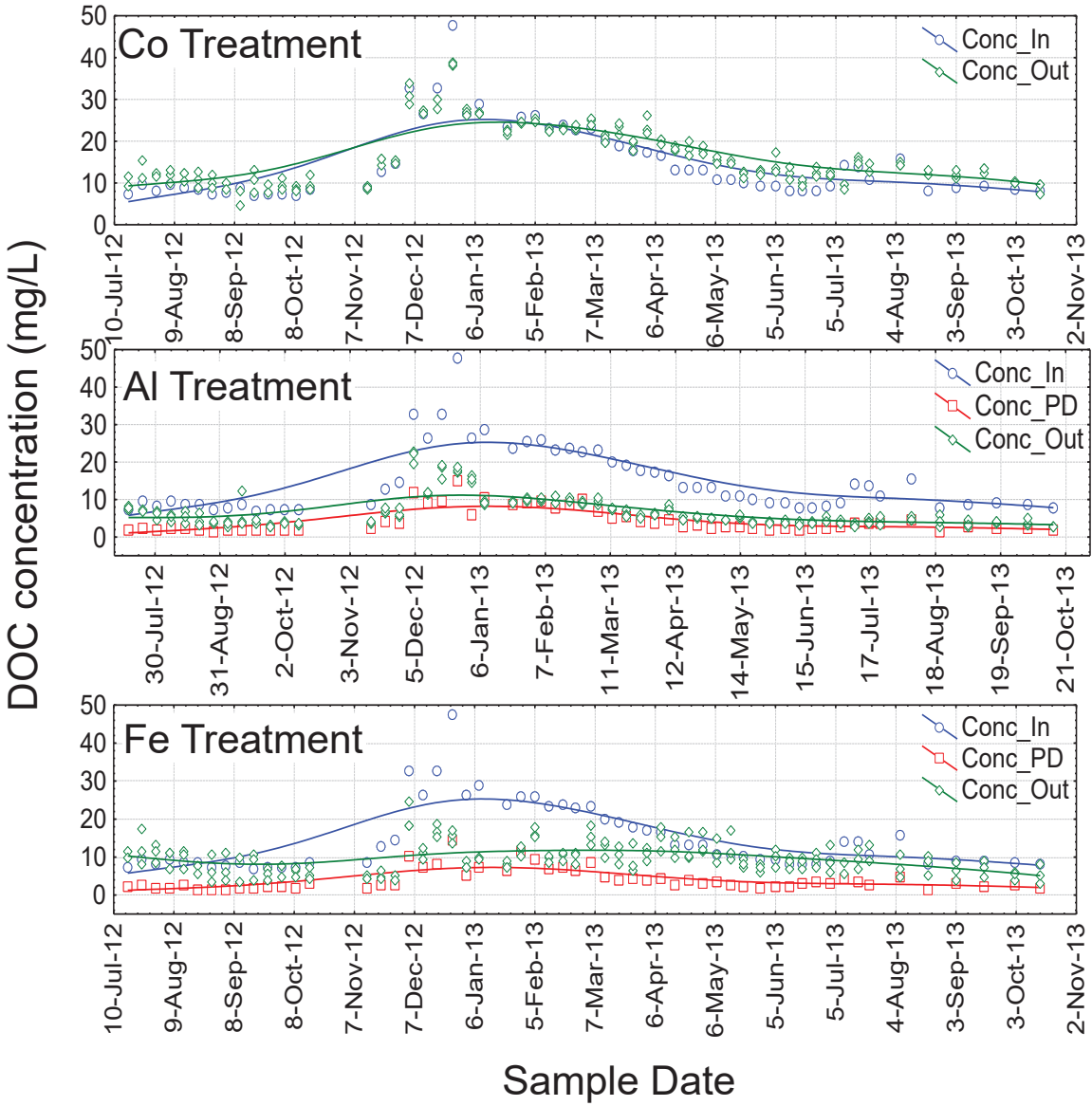
**Figure S1. Plug flow reactor (PFR) kinetic model schematic.**  
 Model describes analyte processes in continuous flowing systems with consideration to precipitation rate ( $Q_p$ ), evapotranspiration rate ( $Q_E$ ), fluid flow rate at relevant temperature ( $Q_T$ ), analyte flow rate ( $Q_x$ ), change in fluid flow rate ( $\Delta Q$ ), change in concentration ( $\Delta C$ ), concentration of analyte ( $C_x$ ) and change in time ( $\Delta t$ ).



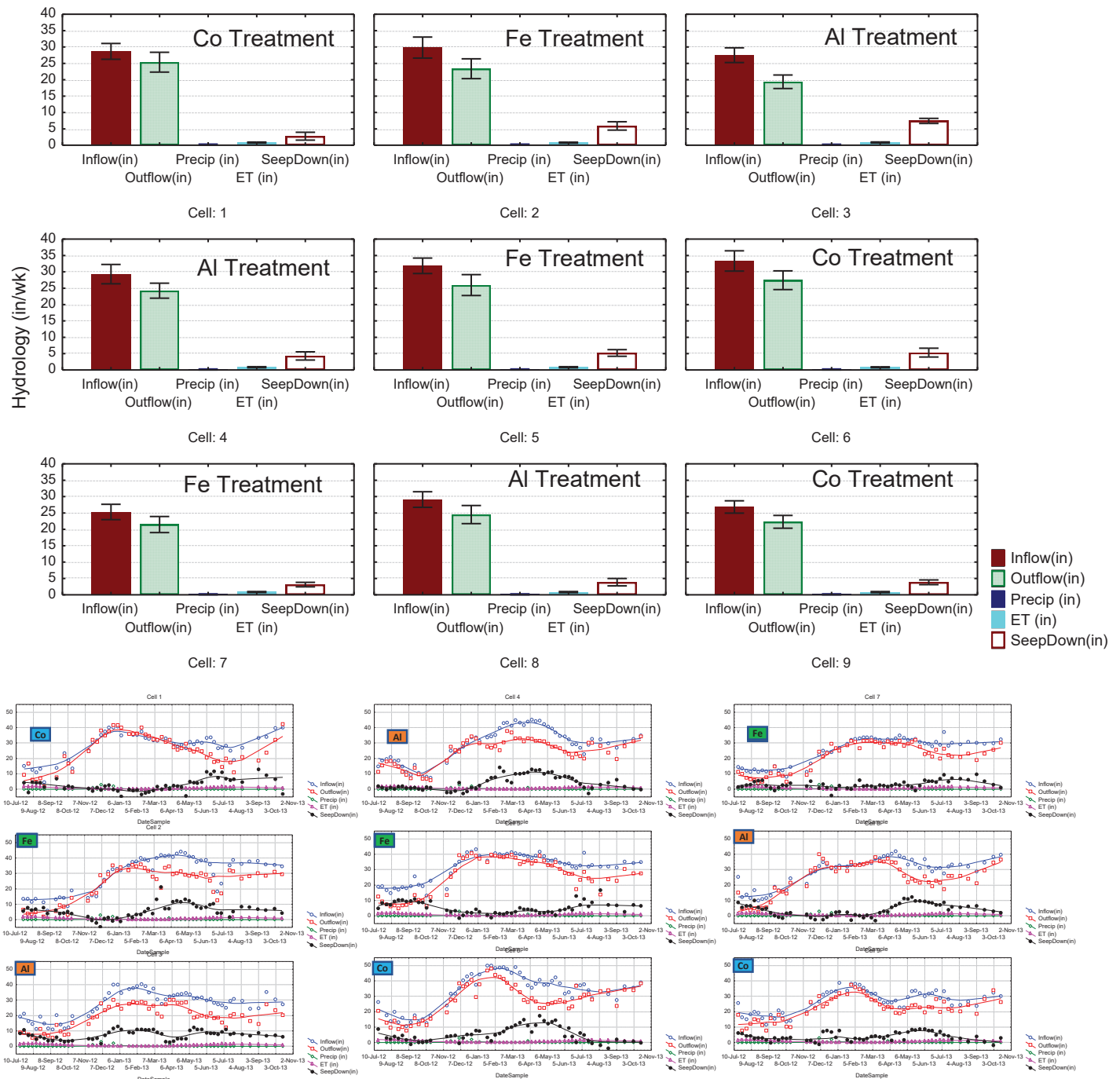
**Figure S2. Release of dissolved organic carbon from coagulated wetlands.** Difference in dissolved organic carbon (DOC) uptake between coagulated [iron (Fe) and aluminum (Al)] and control (Co) treatments versus DOC removed by coagulant (in weekly loads, mg/m<sup>2</sup>wk). Negative numbers indicate DOC release in wetlands. Coefficients of determination (R<sup>2</sup>) and probability values (p) are shown.



**Figure S3. Temporal dissolved organic carbon trends.** Temporal concentrations (mg/L) for dissolved organic carbon (DOC) across the system at the inflow (In), post-dosing (PD) and outflow (Out) locations for Control (Co), aluminum (Al) and iron (Fe) treatments.



**Figure S4. Weekly and seasonal hydrologic water budgets.** Weekly (in/wk) and seasonal (inches) water budgets for all treatment wetland cells showing inflow, outflow, precipitation (Precip), evapotranspiration (ET) and seepage (SeepDown) hydrologic pathways. Water budgets for each cell were calculated daily using average daily inflow, outflow, evapotranspiration (ET) and precipitation. Infiltration losses due to seepage were calculated by difference.



Water budgets developed showed treatment wetland cells experienced a slight downward infiltration gradient as designed through maintaining water levels in nearby drainage ditches below water levels in the cells. On average, about 15% of inflow to the cells was lost to seepage, typically ranging between 10 – 20%. Losses to seepage varied seasonally with higher seepage rates starting during the summer months often extending through autumn to early winter months. Island drain practices partially account for seasonal differences. Greater drain water pumping occurred during the summer to keep groundwater tables lower to accommodate agricultural production (Deverel et al., 2007). Less than 3% of losses were from ET and precipitation accounted for less than 1% of the hydrologic loading to the systems.

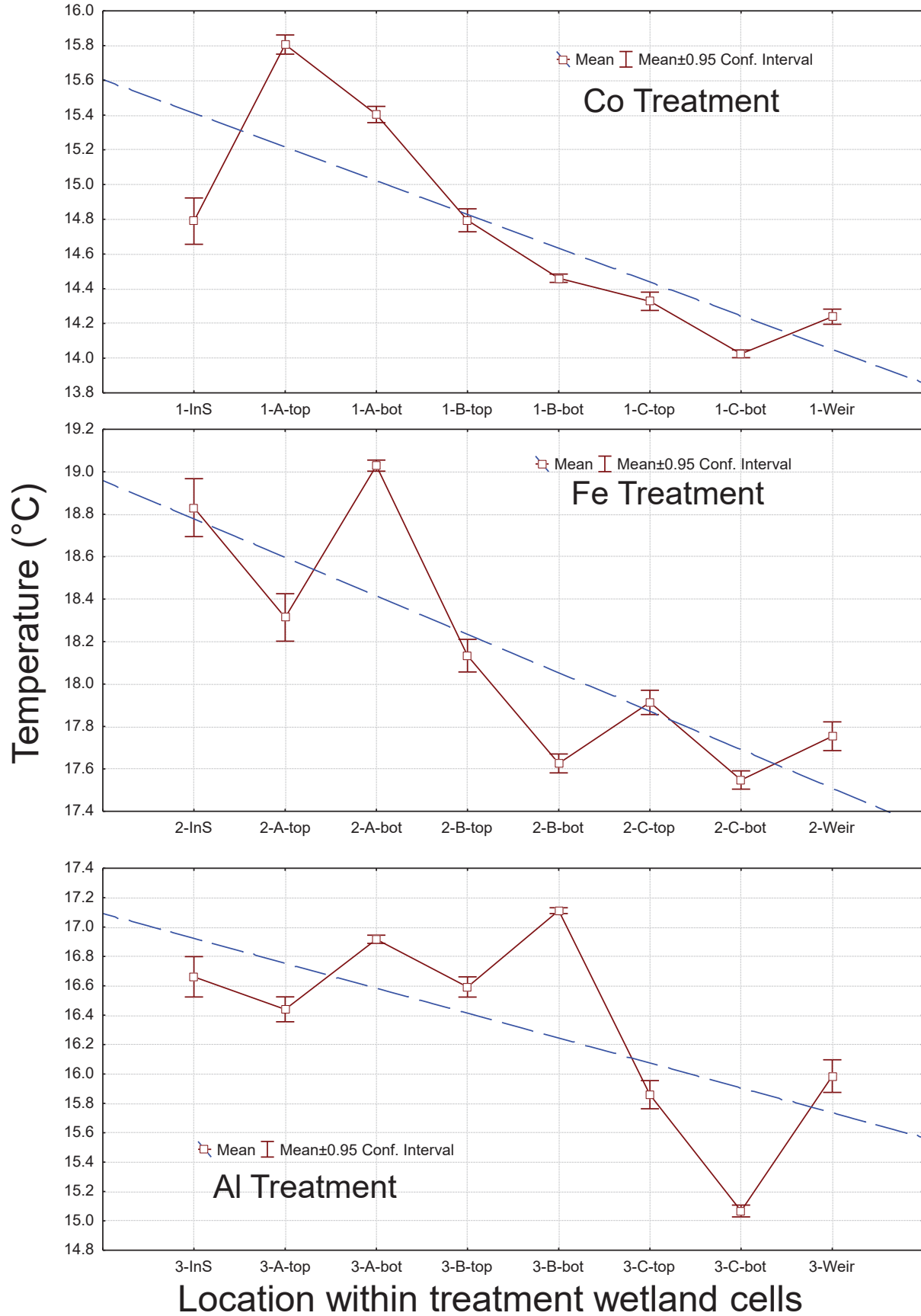


# Synoptic Study

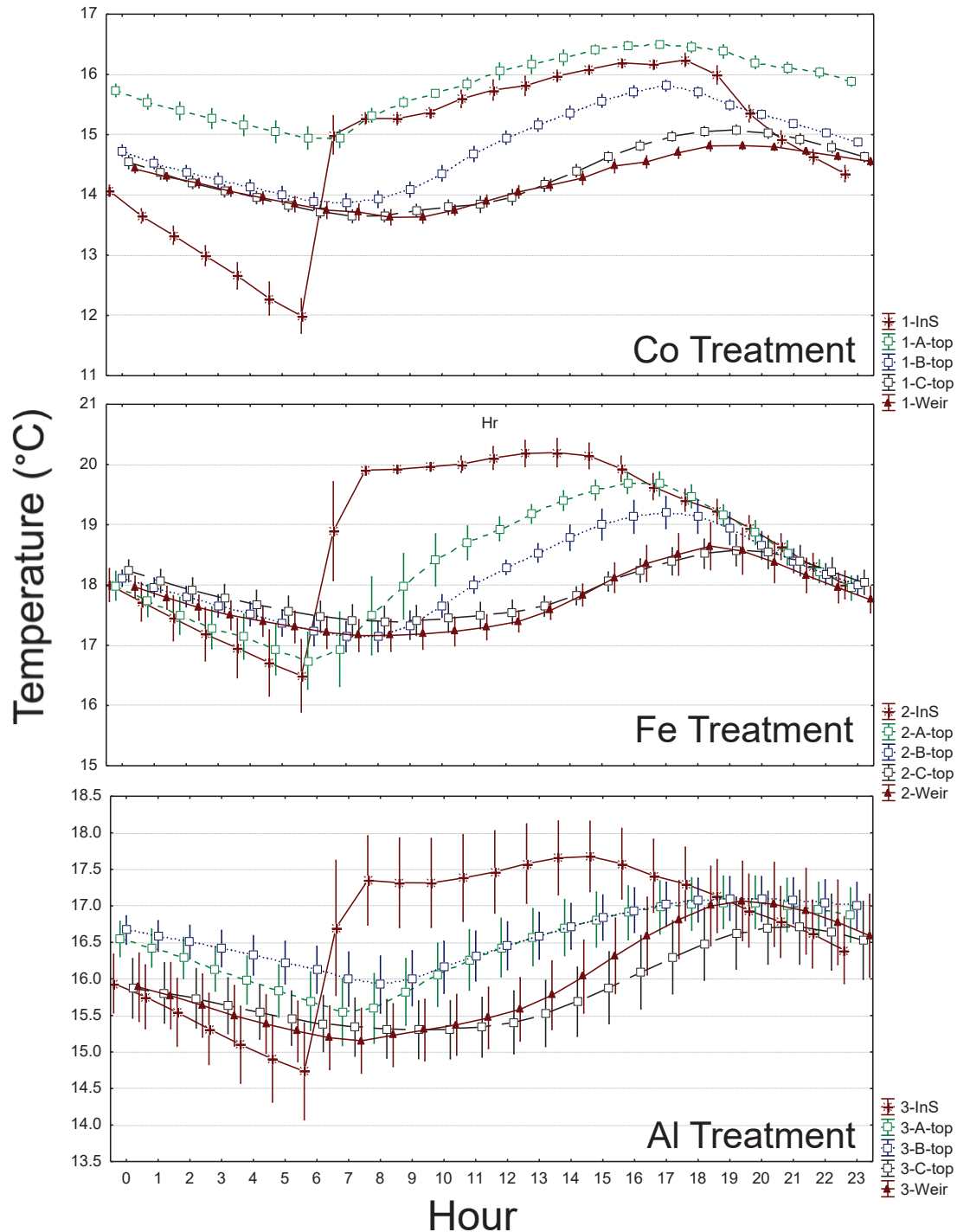
(Figures S5 and S6)

YSI 6920 multi-parameter water quality data-sondes were installed at the inflows, outflows and piers (Figure 1b) near the top (0.91 – 1.2 m below water surface) and bottom (0.91 – 1.2 m above sediment) of the water column for collection of temperature data. One week long synoptic studies were conducted successively in cells 1 (Control), 2 (Fe treatment) and 3 (Al treatment), with placement of the YSI sondes in cell 2 from 9/17 – 9/24/2013, in cell 3 from 9/26 – 10/3/2013 and in cell 1 from 10/8/2013 – 10/15/2013. YSI data was measured at 15-minute intervals.

**Figure S5. Temperature changes along treatment wetland cells.** Temperature ( $^{\circ}\text{C}$ ) changes along wetland gradient (inflow to outflow) for control (Co), iron (Fe) and aluminum (Al) treatments. Means and confidence intervals (Conf. Interval) are shown. YSI measurements were taken at inflow surface (InS), pier A top (A-top), pier A bottom (A-bot), pier B top (B-top), pier B bottom (B-bot), pier C top (C-top), pier C bottom (C-bot) and Weir locations, blue dotted line represents characteristics of ideal plug flow reactor system.

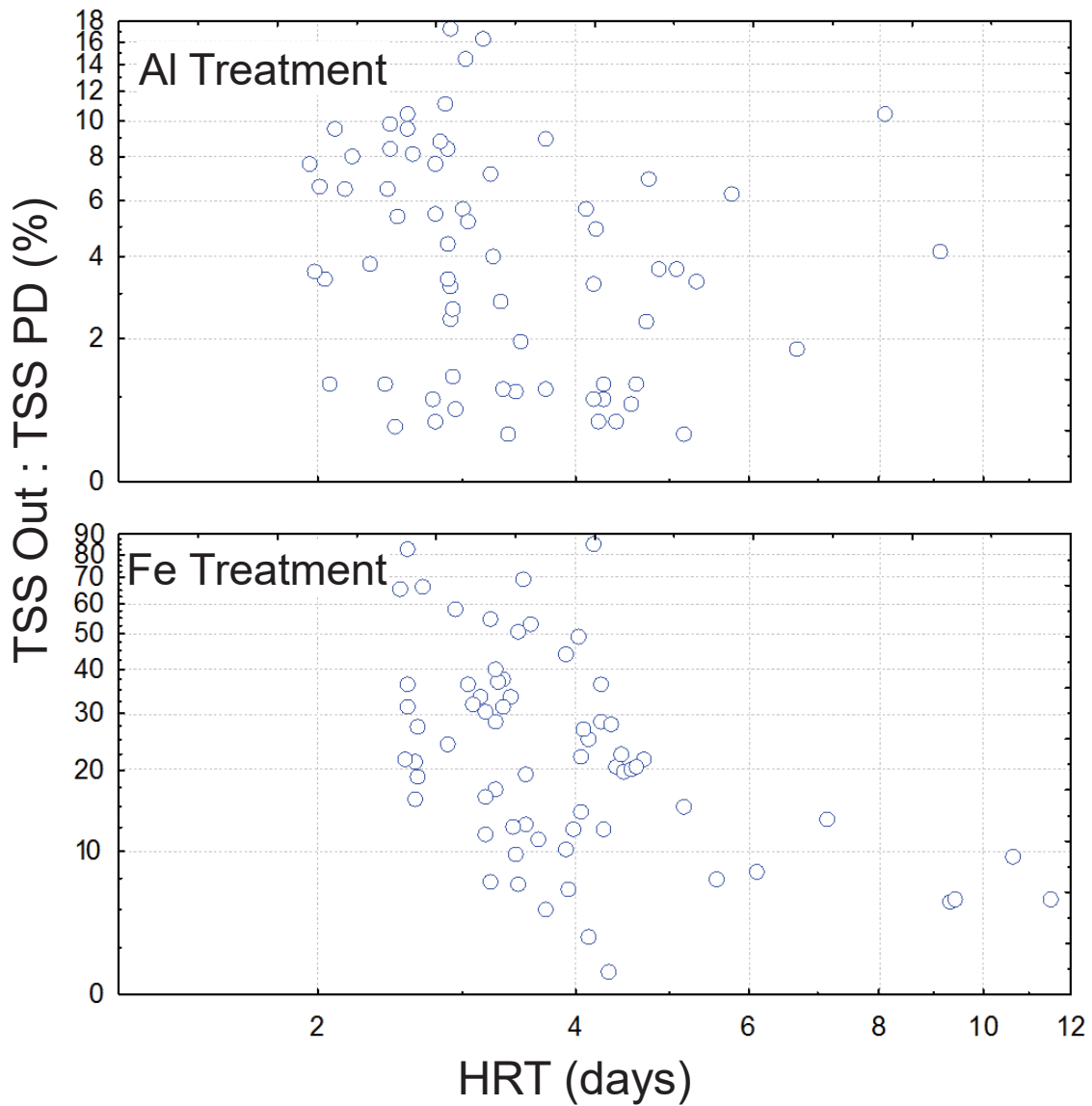


**Figure S6. Temporal temperature in treatment wetland cells.** Daily temporal temperature changes across the wetland cells for Control (Co), iron (Fe) and aluminum (Al) treatments. YSI temperature measurements were taken at inflow surface (InS), pier A top (A-top), pier B top (B-top), pier C top (C-top) and weir locations in control (a), Fe (b) and Al (c) treatments. Temperature ( $^{\circ}\text{C}$ ) means with 95% confidence intervals are shown.

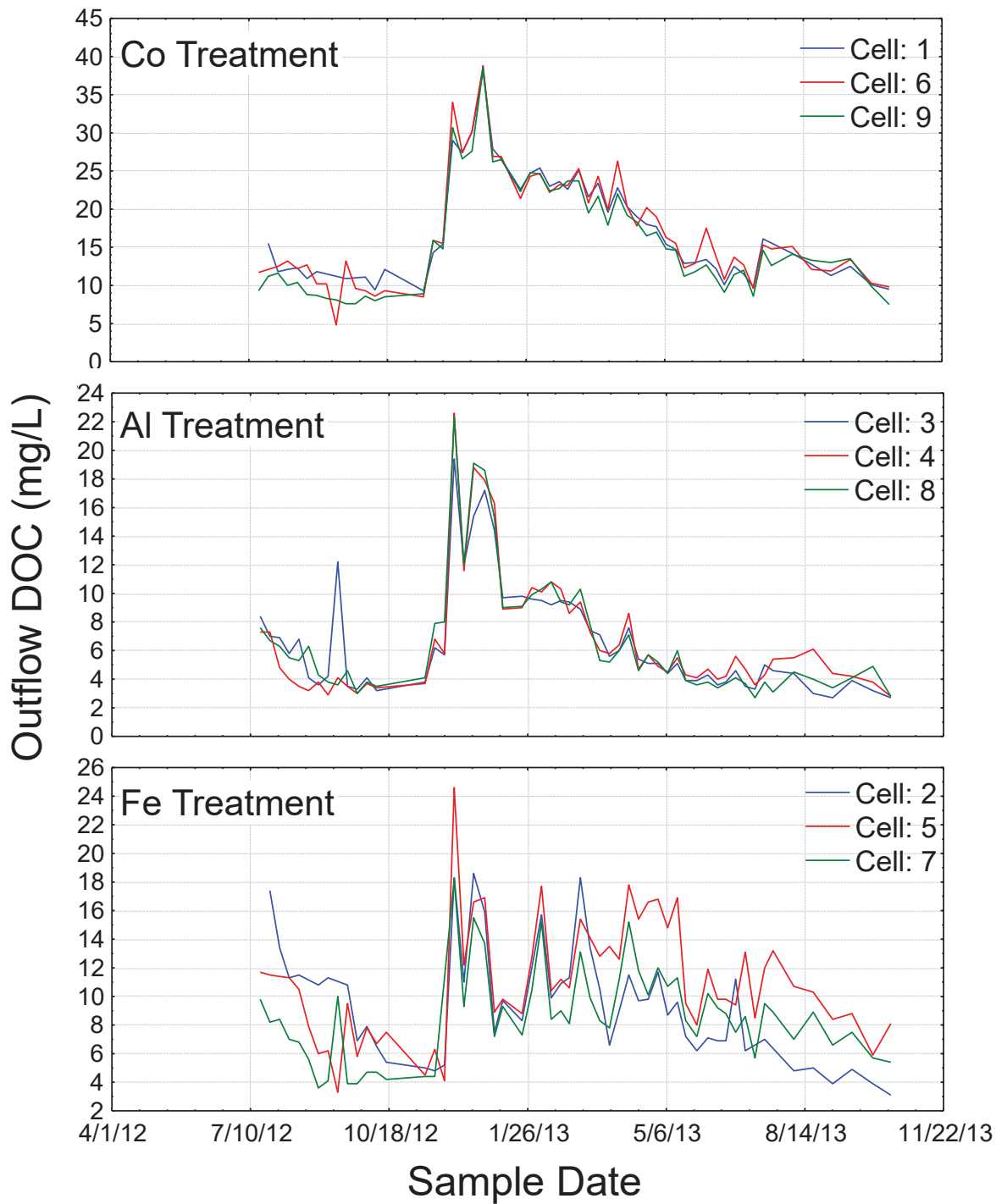


Water, which started flowing into the treatment wetland cells at 6:30 am, immediately warmed at the inflow surface (InS) located near the inflow piping (Figure 5). The warming front then moved through the cell along a downstream gradient. When water stopped flowing into the cells (6:30 pm), the water temperature near the inflow (InS) immediately started dropping; this drop also tends to move along a gradient, although the results are somewhat confounded by the fact that water temperature tends to drop during the evening hours.

**Figure S7. Percent total suspended solids removal by coagulated wetlands.** Outflow (Out) to post-dosing (PD) total suspended solid (TSS) percentage versus hydrologic retention time (HRT) for iron (Fe) and aluminum (Al) treatments. TSS was performed on filtered samples (0.3  $\mu\text{m}$  nominal pore-size glass fiber filters) and measured on weekly water samples gravimetrically after filtration (Eaton et al., 2005).



**Figure S8. Measured outflow dissolved organic carbon concentrations by treatment wetland cell.** Measured outflow dissolved organic carbon (DOC) concentrations (mg/L) from the different replicate wetlands within a treatment. Treatments are indicated by Co, Fe and Al for the Control, iron and aluminum treatments, respectively.



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